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**Hydrothermal decomposition of various crystalline celluloses as treated by
semi-flow hot-compressed water**

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Abstract

Various types of crystalline celluloses I, II, III_I, III_{II}, IV_I and IV_{II} that have been adjusted for their degree of polymerization (*DP*) were treated by semi-flow hot-compressed water (HCW) at 230-270°C/10 MPa/15 min in order to study their chemical decomposition. The treatments resulted in either partial or complete decomposition of the celluloses and the decomposed products were primarily recovered as hydrolyzed, dehydrated and fragmented ones as well as organic acids in the water-soluble (WS) portions. Their results of chemical decomposition and its kinetics revealed that the celluloses decomposition is dependent on the types of crystalline celluloses as well as temperature of the HCW treatment. The outcome from the WS portions at 270°C/10 MPa/15 min showed that the degree of difficulty for decomposition is lower in group II (cell II, cell III_{II}, cell IV_{II}) than group I (cell I, cell III_I, cell IV_I), indicating that group II is less resistant to decomposition by HCW treatment. Therefore, the decomposition behaviors of the cellulose are due to the inherent differences in the crystalline structures.

Keywords Cellulose, Cotton linter, Crystalline structure, Hydrolysis, Semi-flow hot-compressed water

Introduction

Currently, almost all ethanol from renewable carbon is obtained from food-based sources such as starch and molasses. The shortage of capacity and competition from food requirement drives the need for lignocellulose, such as grasses and woods, to serve carbon resources for promising biofuels [1]. Cellulose as one of the main components in lignocellulose with approximate production of 1.5×10^{12} tons each year globally has high potential to be exploited for this purpose [2, 3]. It can be chemically converted into fermentable saccharides, however, this is usually hindered by its great resistance to hydrolysis [4].

Cellulose is a linear crystalline homopolymer consisting of β -1,4-linked D-glucopyranose units. It exists in six known polymorphs of celluloses (I, II, III_I, III_{II}, IV_I, IV_{II}) identified by their characteristic X-ray diffraction (XRD) patterns as well as ^{13}C nuclear magnetic resonance (NMR) spectra. In nature, cellulose has high degree of polymerization (*DP*), in a range of about 6000 to 15000 glucopyranose units [5] which makes it highly crystalline and not easy to be separated or dissolved in almost any solvents [6,7]. Thus, numerous biological, chemical, and/or physical treatments such as enzymatic saccharification, acid/alkali treatments, steam explosion, supercritical and subcritical treatments have been applied and developed for cellulose hydrolysis [8-14].

Hydrothermal treatment in hot-compressed water (HCW) has been proposed as a promising method to hydrolyze cellulose mostly due to its non-toxic, non-catalytic and environmentally benign properties [15-18]. Furthermore, over conventional method, it has advantages such as limited corrosion problem, no sludge generation, low capital and operational cost, as well as no significant degradation of cellulose at normal operating conditions [19]. The conventional methods such as acid/alkali treatment and acid/alkali pretreatment followed by enzymatic hydrolysis are associated with serious economic and environmental constraints due to the heavy use of chemicals.

Hot-compressed water is highly pressurized, high temperature liquid water at subcritical condition, below the critical point of water at $374^\circ\text{C}/22.1 \text{ MPa}$ [20]. It is characterized by a higher ionic product and thus higher concentration of H^+ and OH^- ions, compared to ambient water, offering a highly interesting reaction medium for hydrolysis processes. In addition, acid neutralization is not required because the concentration of H^+ ion is a function of temperature, and decreases when the temperature is lowered. Many studies have confirmed that cellulose can be largely hydrolyzed in subcritical water without addition of a catalyst [21-26].

The experimental results using a flow-type HCW treatment showed that glucose yield increases with increasing temperature [27]. It has less significant degradation reactions as compared with batch-type treatment that makes it preferable for hydrolysis process of lignocellulose [28-30]. It has been reported that 4-22 % of cellulose could be hydrolyzed by flow-type HCW treatment (200-230°C/34.5 MPa/15 min) [31].

To the best of authors' knowledge, studies have been done on analysis of cellulose hydrolysis by using HCW treatment; however, the comprehensive investigation has been rarely conducted on various crystalline celluloses as feedstocks. The physical characteristics such as crystallinity and *DP* of various crystalline cellulose residues as treated by semi-flow HCW were thoroughly explored in previous study together with a brief evaluation on the water-soluble (WS) portions [32]. Therefore, as a further approach, the primary objective of this work is to study quantitatively the chemical decomposition from various crystalline celluloses as treated by semi-flow HCW through the yields of WS portions.

Materials and Methods

Preparation of various types of crystalline cellulose samples

Cotton linter (Buckeye 1AY-500), in the form of cellulose I (cell I), was used to prepare various types of crystalline celluloses. Cellulose II (cell II) was prepared from cell I through mercerization by soaking it into 20.0 % of aqueous NaOH solution for 24 h at ambient condition of temperature (20°C) and pressure (0.1 MPa), followed by washing thoroughly with water and freeze-drying [33]. As for celluloses III_I (cell III_I) and III_{II} (cell III_{II}), they were prepared from cell I and cell II, respectively. Cell I and cell II were soaked in 100 % ethylenediamine for 24 h at ambient condition, washed with dried methanol and kept under vacuum.

The prepared cell III_I and cell III_{II} were further used for the preparation of celluloses IV_I (cell IV_I) and IV_{II} (cell IV_{II}), by firstly soaking them in glycerol for 3 d at ambient condition. They were then heated in a reaction vessel at 260°C/0.6 MPa for 30 min and cooled down to ambient condition [34]. The product was, then, washed with water and acetone successively, and dried in vacuum. Basically, the converted celluloses consisted of group I (cell I, cell III_I, cell IV_I) and group II (cell II, cell III_{II}, cell IV_{II}). Their chemical compositions were also analyzed and all these celluloses were found to contain similar monosaccharide components of about 99.9 wt% glucose and 0.1 wt% xylose [35].

To compare the decomposition products from the water-soluble (WS) portions on various types of crystalline celluloses by semi-flow HCW treatment, cellulose with similar

DP are necessary for their evaluation. Consequently, these celluloses were adjusted by trial and error for their *DP*s by changing the treatment condition mentioned above for converting cell I to various forms of celluloses.

The determination of *DP* and crystallinity of the celluloses

The celluloses were dissolved in 0.5 M cupriethylenediamine (Cuen) by viscometry as per TAPPI method [36]. The *DP* of the celluloses was then calculated from the intrinsic viscosity $[\eta]$ according to the equation $DP^{0.905} = 0.75[\eta]$ [37]. For the crystallinity determination, Gaussian functions were used to deconvolute the XRD patterns of various crystalline celluloses [38]. These XRD patterns were recorded by X-ray diffractometer Rigaku RINT 2200 [32].

Treatment of various crystalline cellulose samples by semi-flow HCW treatment

The prepared celluloses as starting materials were then treated individually in a semi-flow HCW system. The conversion system and its operational procedures as explained elsewhere were adapted for this study [24-26]. Briefly, about 0.4 g of cellulose was treated individually within a 5 mL reaction vessel. The ambient distilled water from a water tank was flown through the reaction vessel by a pump in order to pressurize the system at 10 MPa controlled by a back-pressure regulator. To raise the temperature, the preheating unit monitored by thermocouples was used to reach at the designated temperatures of 230, 250 and 270°C for about 20 min under 10 MPa and remain constant for additional 15 min, totally 35 min. In addition, another heating unit was installed at the reaction vessel to maintain the designated temperature in the reaction vessel, into which the HCW was passed through at the flow-rate of 10 mL/min.

These treatments yielded insoluble residues [32] and WS portions. After the HCW passing through the reaction vessel, the WS portions were cooled down immediately by the cooling system to terminate all reactions and collected every 5 min. They were allowed to settle in ambient temperature and pressure for a minimum of 12 h. Though no precipitation was observed after at least 12 h, it was filtered by 0.45 μ m membrane prior to the subsequent analyses.

Analytical methods

The WS portions collected were analyzed and characterized by using high-performance anion exchange chromatography (HPAEC), high-performance liquid

chromatography (HPLC) and capillary electrophoresis (CE). The HPAEC system (Dionex ICS-1000 system) equipped with the CarboPac PA-1 column (4 mm x 250 mm) and electrochemical detector for pulsed amperometric detection was employed and operated at 35°C and flow-rate of 1.0 mL/min under the helium atmosphere for monosaccharides and cello-oligosaccharides in the WS portions. The mobile phase was a gradient-programmed mixture of deionized water, 0.2 M NaOH and 2.0 M CH₃COONa, as eluents. All eluents contained in 3 separate reservoirs were degassed by an aspirator and subsequently purged with helium to prevent the absorption of CO₂.

The HPLC system (Shidmadzu, LC-10A) equipped with a Shodex Sugar KS-801/Ultron PS-80P columns and refractive index/UV-Vis detector was applied. The eluent used was deionized water at a flow-rate of 1.0 mL/min and oven temperature was set to be 80°C for the columns. The CE (Agilent; Germany) was used to assay the low molecular weight organic acids. A fused-silica capillary (Agilent; 75 µm diameter, 104 cm total length, 95.5 cm effective length) was used at 15°C.

Concentrations of the products in the WS portions were calculated based on the peak areas on chromatograms obtained from HPAEC, HPLC and CE. A set of standards with known concentrations, containing the compounds that were to be identified both quantitatively and qualitatively, was prepared and analyzed together with the samples by using the relevant analytical equipment as mentioned above [18, 24, 25].

Results and Discussion

To investigate the decomposition behaviors on various types of crystalline celluloses by semi-flow HCW treatment, the celluloses must have the same *D*P_s as the starting materials. Thus, a direct comparison between the celluloses is feasible, as listed in Table 1. Treatments by semi-flow HCW were then carried out for these celluloses at temperatures of 230, 250 and 270°C under 10 MPa for 15 min (230-270°C/10 MPa/15 min).

Decomposition kinetics

The semi-flow HCW treatment decomposed various crystalline celluloses either partially or completely to the WS portions. The yield on WS portions from various crystalline celluloses as shown in Fig. 1, is a function of treatment temperatures. At constant treatment time, the yield on WS portions increased as the temperature increased. They were measurable even at lower temperature, 230°C/10 MPa, with approximately 10-30 wt% and increased to more than 70 wt% at higher temperature, 270°C/10 MPa. At 270°C/10 MPa/15 min, cell II

was shown to be totally decomposed to WS portions as compared with other celluloses. The overall results from Fig.1 illustrated that higher yields were obtainable for group II celluloses than group I.

Figure 2 shows the Arrhenius plot of the present results according to the pseudo-first-order reaction kinetics. The relationship between natural logarithms of reaction constants, $\ln k$, and T^{-1} shows good linear fits with the results indicating that the decomposition follows the pseudo-first-order reaction kinetics. Every parameter used such as time, pressure and DP on the celluloses were kept constant, satisfying the assumption that the Arrhenius-plot is temperature dependent. Though, the data points obtained in this study are only based on three different temperatures profile, the degree of decomposition could be determined reliably and the comparison of kinetics on various crystalline celluloses can be done directly.

The apparent activation energies, E_a , for the celluloses can be calculated from Fig. 2. Activation energy of any reaction mainly explains its degree of temperature-sensitiveness; reactions with higher E_a are high in temperature-sensitiveness, while the reactions with lower E_a are low temperature-sensitive [39]. It can also be said that E_a is defined as the minimum energy required for decomposition to occur. The smaller E_a for decomposition of cellulose signifies the requirement of less energy for its decomposition and *vice versa*. In Fig.2, it was shown that different slopes obtained for each of the celluloses suggested different E_a for cellulose decomposition in the studied temperature range.

Table 2 shows the obtained E_a for all celluloses within the treatment temperatures. The E_a for group I and group II celluloses are, respectively, greater than 70 kJ/mol and in between 50-60 kJ/mol. It is apparent that the celluloses in group I have higher E_a than those in group II, which implies an easier decomposition process for group II celluloses by semi-flow HCW treatment. However, due to the aforementioned limitations such as limited numbers of experiments carried out in a relatively narrow temperature range, the obtained E_a must be judged critically. The acquired E_a was based on the best fit curves. As a result, a higher E_a was obtained for cell IV_I as compared with cell I and cell III_I. Since comparison of E_a was done between group I and group II, the above observation of group I having higher E_a than group II is valid.

These E_a are lower than previously reported, 164 kJ/mol [7] and 145 kJ/mol [40] without catalysts, whereas, 144 kJ/mol and 100 kJ/mol [41] in dilute sulfuric acid catalyst. The differences in E_a could be due to various definitions of decomposition processes and treatment conditions used. For instance, Sasaki et al. [40] studied just the kinetics of cellulose

hydrolysis only at elevated temperatures (above 290°C/25 MPa), whereby in this work the kinetics of various cellulose decomposition was measured at 230-270°C/10 MPa.

Here, the observed decomposition of cellulose in subcritical water appears to be as good as that occurring in dilute sulphuric acid hydrolysis [41]. Cellulose firstly undergoes a rapid weight loss and followed by a slow hydrolysis step of the remaining cellulose. The high reactivity is associated with accessible amorphous regions in cellulose that are more vulnerable to chemical attacks than the crystalline regions [42]. The reaction temperature has influence on the solvent properties of water [15, 43]. It has been suggested that the shift in solvent properties affects the kinetics of cellulose decomposition [44, 45]. However, in this present work, the constant E_a implies that the reaction mechanism of the hydrothermal decomposition is not distinctly affected. The lower E_a obtained indirectly showed that the decomposition of various celluloses in this system is a catalytic process, in agreement with the literature [41].

Quantification of water-soluble (WS) portions

Figure 3 shows the reaction scheme of cellulose I decomposition into hydrolyzed and degraded products as treated by semi-flow HCW treatment, adapted from [32]. In the present work, the WS portions for various crystalline celluloses obtained from each treatment were found to follow a similar decomposition pathway as in Fig. 3. It is important to know the decomposition pathway of cellulose as the degraded products inhibit the fermentation process for ethanol production [46].

Under the HCW conditions, the ionization constant of water increases with temperature and the amount of dissociation also increases, compared with normal temperature and pressure. The glucosidic linkages of cellulose are cleaved and cellulose starts to hydrolyze into cello-oligosaccharides, and subsequently, hydrolyzed to monosaccharide of glucose [20, 25, 47, 48]. Isomerization of glucose occurred producing fructose and mannose. These monosaccharides are unstable at high temperature and thus some parts of them are further converted into their degraded products such as furfural, 5-hydroxymethyl furfural (5HMF), levoglucosan through dehydration, and erythrose, glycolaldehyde, methylglyoxal through fragmentation [49]. Prolonged treatment, however, allows further degradation to take place, generating other products such as organic acids.

The resulted WS portion percentages based on the dried weight of cellulose samples clearly indicated that the celluloses have been converted to the hydrolyzed and degraded products. The hydrolyzed products are comprised of cello-oligosaccharides, glucose, fructose

and mannose, whereas the degraded products consist of dehydrated and fragmented products, as well as organic acids. Their productions were recorded higher in hydrolyzed products as compared with degraded products, and more yields were obtained as treatment temperatures increased.

These WS portions were calculated similarly as in the previous studies [24, 25]. The cello-oligosaccharides were consisted of cellobiose, cellotriose, cellotetraose, cellopentaose, cellohexaose and other cello-oligosaccharides with the higher *DP*. The more existence of the cello-oligosaccharides with the higher *DP* shows that the cellulose has more resistance against hydrolysis by semi-flow HCW treatment. In addition to cello-oligosaccharides and glucose, a smaller amount of fructose was also detected and only traces of mannose were identified.

A much lower yield of the WS portions obtained at 230°C/10 MPa/15 min (data not shown) was due to the difficulty of the crystalline structures of celluloses to be hydrolyzed at such lower temperature [26]. The cello-oligosaccharides observed could be obtained from the paracrystalline cellulose. The observed fructose is not a sugar component in cotton linter, but it may be isomerized from glucose after hydrolysis from cellulose [50, 51].

To evaluate the decomposition behavior of various crystalline celluloses in details, the results from 270°C/10 MPa/15 min would be more appropriate, as at this condition, crystalline cellulose is known to decompose [20, 25, 26]. Table 3 shows the comparison between hydrolyzed and degraded products for the two groups of cellulose samples at 270°C/10 MPa/15 min. It can be seen that for both group I and group II celluloses, more than 50 wt% of hydrolyzed products were obtained as compared with degraded products. It was reported that about 31.2, 28.1 and 20.5 wt% of hydrolyzed products obtained from the cellulose of Japanese cedar, Japanese beech and Nipa frond, respectively [52]. However, there were no results for *DP* of the cellulose from this study that it can be compared with. The higher yield in WS portions observed in this present work could probably due to the shorter *DP* celluloses used for the starting materials.

According to Fig. 3, the hydrolyzed products were produced at the early stage of cellulose decomposition pathway. This could signify that these celluloses have resistance against decomposition. The total hydrolyzed products for cell I and cell III_I is similar but much lesser than cell IV_I, whereas the highest hydrolyzed products obtained in group II is from cell III_{II}, followed by cell IV_{II} and cell II. Overall, celluloses in group II have resulted more hydrolyzed products than those in group I. The observation is similar for the degraded products.

Figures 4 and 5, respectively, illustrated how the hydrolyzed and degraded products were obtained at every 5 min intervals at 270°C/10 MPa/15 min. In Fig. 4, only the yields of cello-oligosaccharides, glucose and fructose were shown. These yields are comparable with the results in the literatures [20, 24-26]. Based on these results, the cellulose has been cleaved into cello-oligosaccharides at the early stage of the treatment time and the production of glucose and fructose was seen to occur simultaneously. Celluloses in both group I and group II have similar behaviors; however, more products were seen from group II celluloses. The cello-oligosaccharides and glucose were recovered from the treatment time of 35 min. The crystalline structure of cellulose remained unchanged at temperatures around 230°C [53], thus, the WS portions emerged from the time-up (0-20 min treatment time) could be from paracrystalline cellulose, and the time-at (20-35 min treatment time) was from cellulose.

Generally, these monosaccharides are further degraded by dehydration or fragmentation process [15, 24, 54, 55]. Figure 5 illustrated more dehydrated products were obtained than fragmented products and organic acids. During the treatments, it can be seen that the degraded products were generated at almost similar time as the hydrolyzed products (Fig.4). Moreover, the productions of dehydrated and fragmented products as well as organic acids were generated concurrently. Both group I and group II celluloses in Fig.5 have the same trends as in Fig. 4, i.e., more products resulted from group II celluloses. The generation of hydrolyzed products started to be noticeable from around 3 min (Fig. 4) and followed by degraded products (Fig. 5) about 10 min later. This sequence is parallel with that shown in Fig. 3 at which the hydrolyzed products were produced earlier in the decomposition pathway, and later on followed by the production of degraded products.

Figure 6 shows the yield in wt% for the individual degraded products in the WS portions for both group I and group II celluloses as treated by semi-flow HCW at 270°C/10 MPa/15 min. The dehydrated products detected were consisted of furfural, 5HMF and levoglucosan, whereas fragmented products such as erythrose, glycolaldehyde and methylglyoxal. While for organic acids, acetic, formic, lactic and glycolic acids were identified. The furfural in Fig. 6 can not only be produced from pentose but also from hexose such as glucose. This means that the formation of furfural is possible without pentose via five-carbon ketoses pathway as proposed in the literature [56].

Glycolaldehyde and erythrose were formed via retro-aldol condensation in glycolaldehyde/erythrose pathway [44, 51], while methylglyoxal was produced via glyceraldehyde/dihydroxyacetone pathway in hexose fragmentation. Nevertheless, the production of methylglyoxal in this case was too minute that it was excluded from Fig.6. The

production of furfural and 5HMF was significant as compared with other degraded products. The organic acids produced are the results of further degradation of dehydrated and fragmented products [51, 57]. Lactic acid production was only a trace to be included in Fig. 6. All the sequences of degradation reactions and productions are agreeable with Fig. 3.

Based on those results above, it can be seen that group II celluloses dominated both the hydrolyzed and degraded products as compared with group I celluloses. The result on the WS portions at 270°C/10 MPa/15 min revealed that the degree of difficulty for decomposition is greater for celluloses in group I than those in group II.

Conclusion

This study reveals the essential effects of various crystalline celluloses on their chemical decomposition and its kinetic behaviors as treated by semi-flow HCW. Both decomposition rate and E_a are helpful in defining the degree of difficulty for decomposition of various crystalline celluloses, however, the E_a obtained were merely based on empirical relationships of Arrhenius equation. Consequently, the direct method is more preferable than the latter. Nevertheless, this study showed the new kinetic data as there was no previous data on these specific reaction systems.

These treatments can be used as viable decomposition media for celluloses at which under the given treatment conditions, cellulose is more readily hydrolyzed with less degraded products. Group I celluloses (cell I, cell III_I, cell IV_I) have shown to have more resistance to decompose than group II celluloses (cell II, cell III_{II}, cell IV_{II}). Based on this evidence, it was clear that the decomposition behaviors are due to the different crystalline forms of celluloses. Therefore, it is recommended to transform cellulose I to the other for a better hydrolysis reaction. These presented data are useful for understanding how various types of crystalline celluloses are chemically decomposed, providing useful insights to efficient utilization of lignocellulose for biofuels and biochemicals.

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540 **List of figure captions**

541

542 **Fig. 1** The yield on WS portions from various types of crystalline celluloses as treated at
543 different temperatures under 10 MPa for 15 min (230-270°C/10 MPa/15 min) by semi-flow
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545

546 **Fig. 2** The Arrhenius plot for various crystalline celluloses using pseudo-first order reaction
547 kinetics as treated by semi-flow HCW at 230-270°C/10 MPa/15 min

548

549 **Fig. 3** Decomposition pathway of crystalline cellulose I as treated by semi-flow HCW

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551 **Fig. 4** The hydrolyzed products of cello-oligosaccharides, glucose and fructose in the WS
552 portions from various types of crystalline celluloses as treated by semi-flow HCW at
553 270°C/10 MPa/15 min. Top figure corresponds to treatment temperature (*open squares*)

554

555 **Fig. 5** The degraded products of dehydrated, fragmented and organic acids products in the
556 WS portions from various types of crystalline celluloses as treated by semi-flow HCW at
557 270°C/10 MPa/15 min. Top figure corresponds to treatment temperature (*open squares*)

558

559 **Fig. 6** The degraded products in WS portions from various types of crystalline celluloses as
560 treated by semi-flow HCW at 270°C/10 MPa/15 min

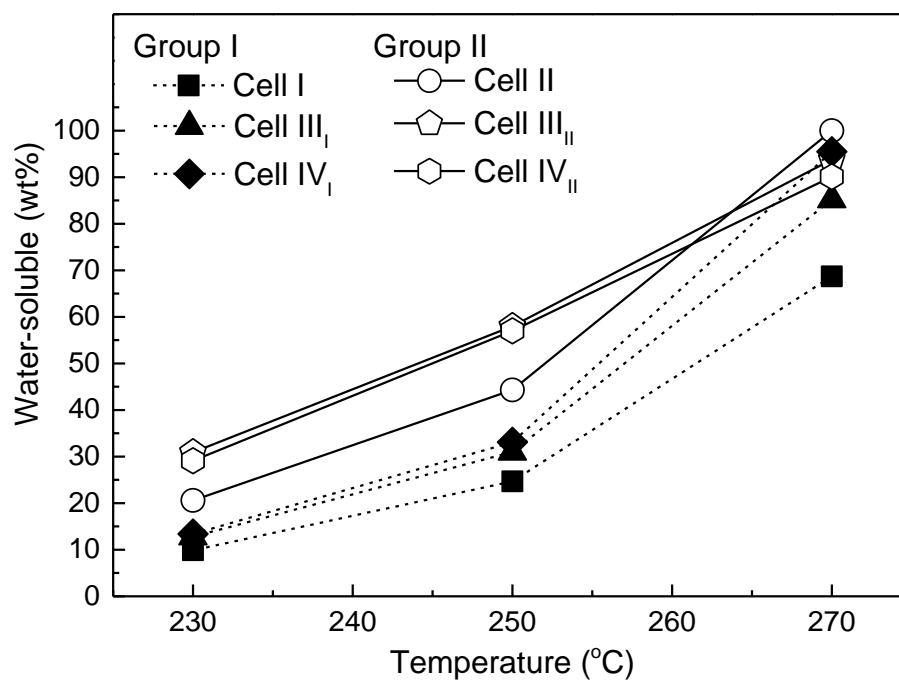


Fig. 1 The yield on WS portions from various types of crystalline celluloses as treated at different temperatures under 10 MPa for 15 min (230-270°C/10 MPa/15 min) by semi-flow HCW

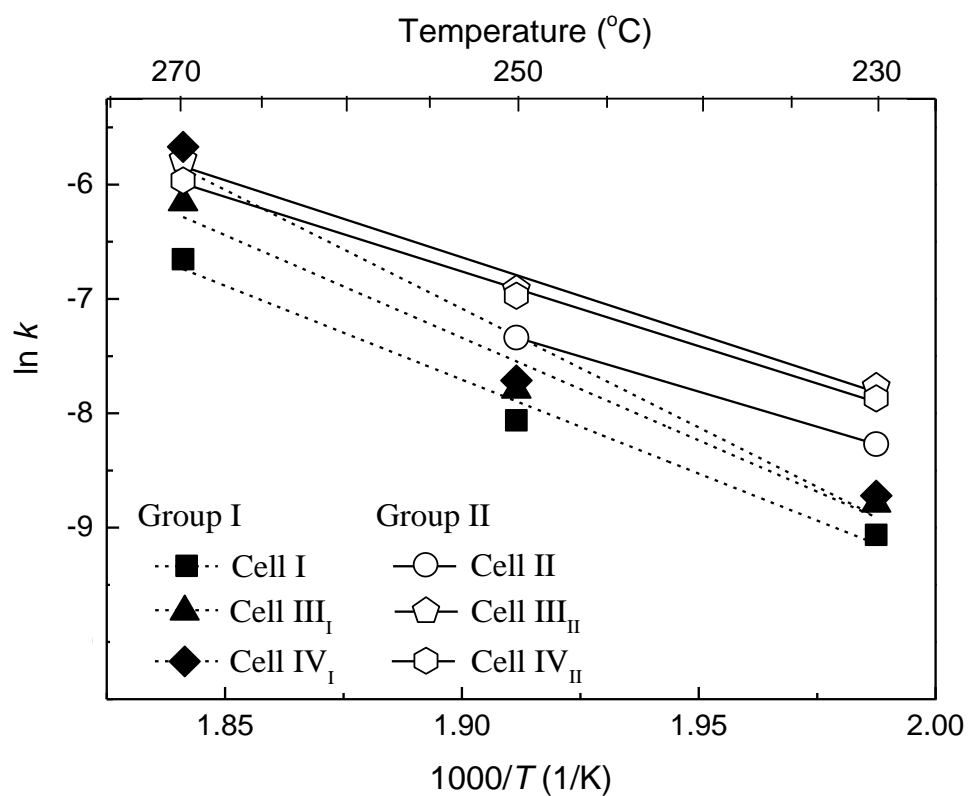


Fig. 2 The Arrhenius plot for various crystalline celluloses using pseudo-first order reaction kinetics as treated by semi-flow HCW at 230-270°C/10 MPa/15 min

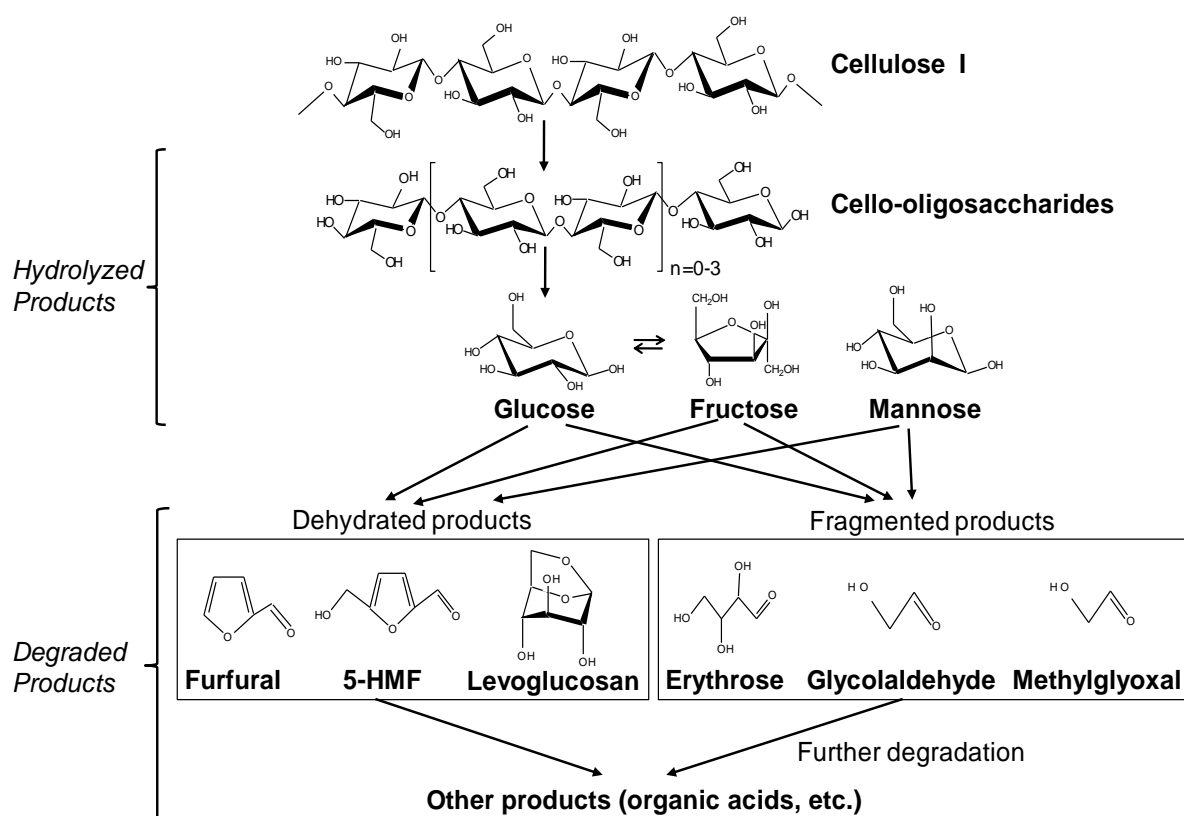


Fig. 3 Decomposition pathway of crystalline cellulose I as treated by semi-flow HCW

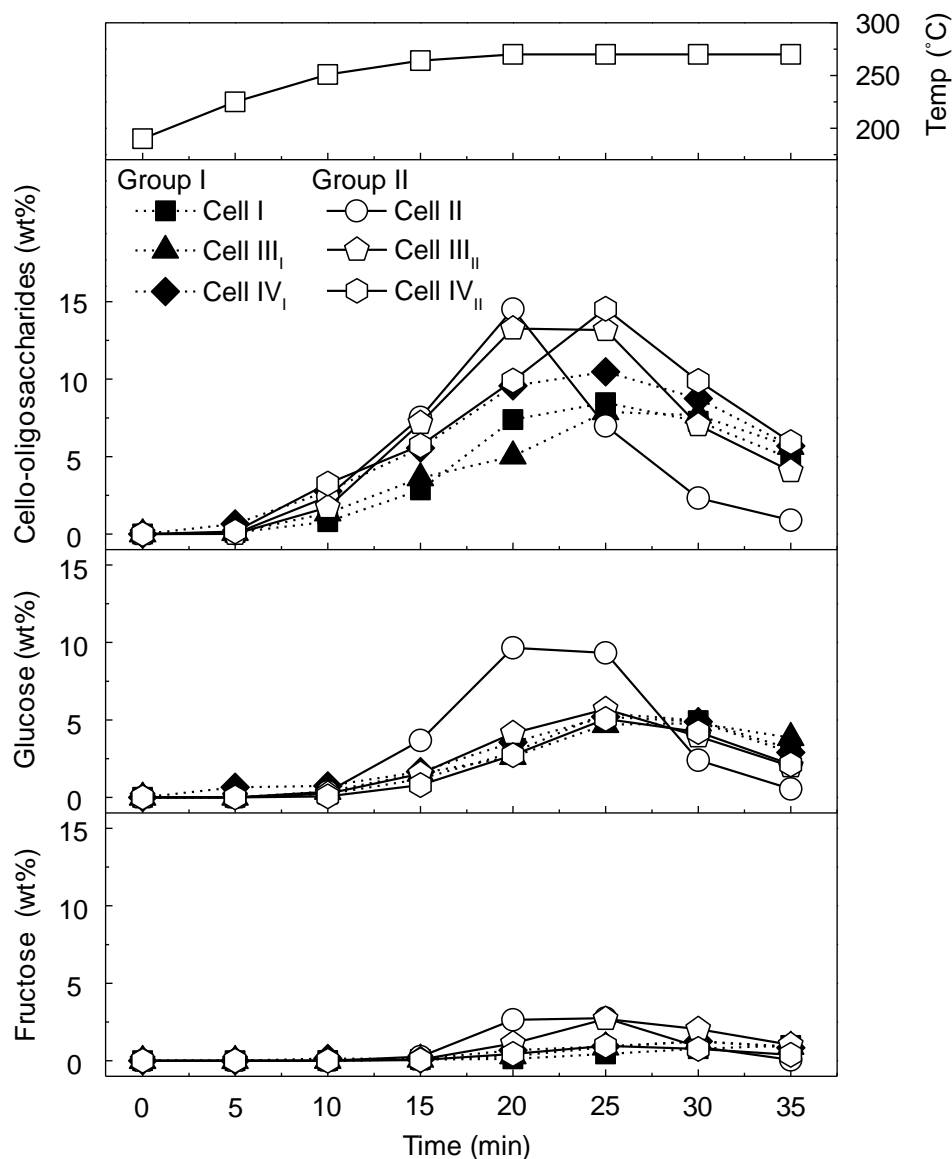


Fig. 4 The hydrolyzed products of cello-oligosaccharides, glucose and fructose in the WS portions from various types of crystalline celluloses as treated by semi-flow HCW at 270°C/10 MPa/15 min. Top figure corresponds to treatment temperature (*open squares*)

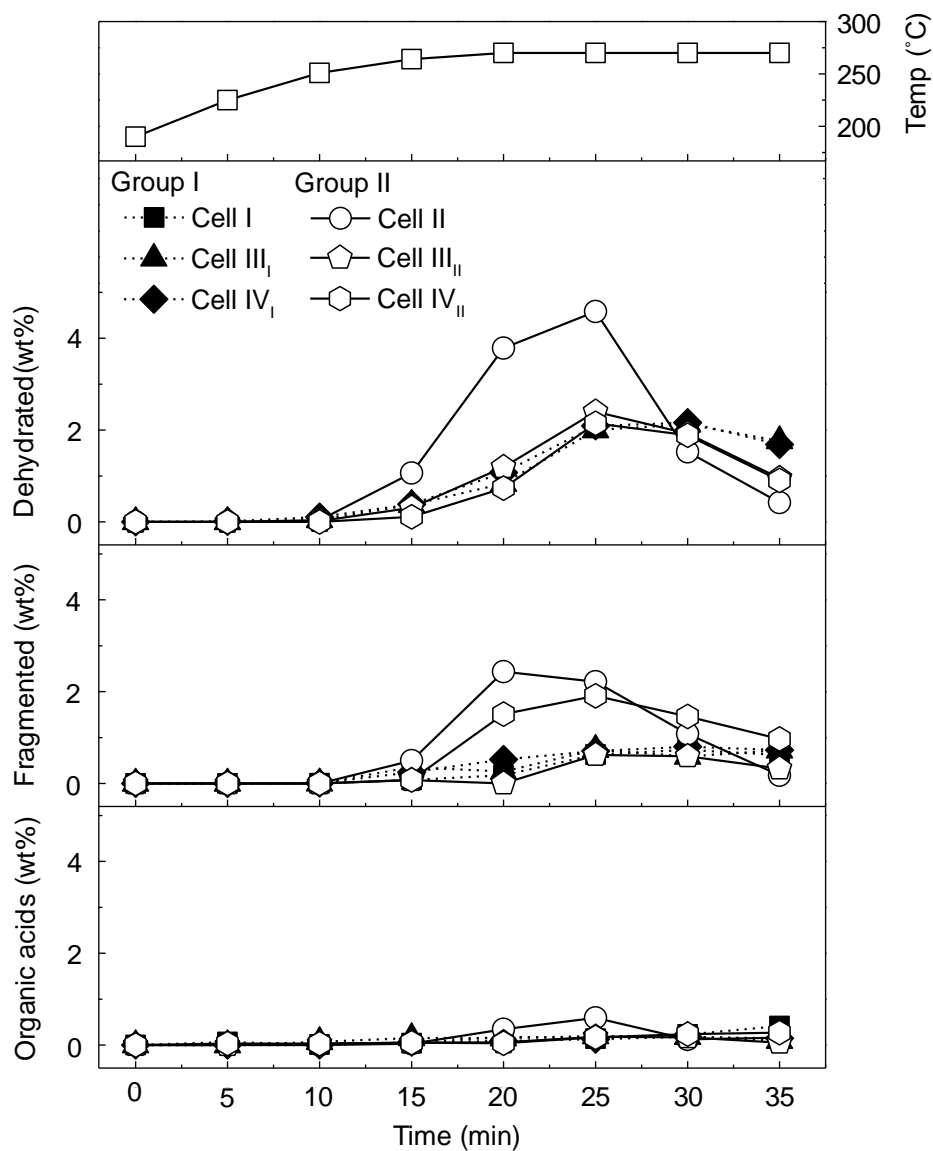


Fig. 5 The degraded products of dehydrated, fragmented and organic acids products in the WS portions from various types of crystalline celluloses as treated by semi-flow HCW at 270°C/10 MPa/15 min. Top figure corresponds to treatment temperature (*open squares*)

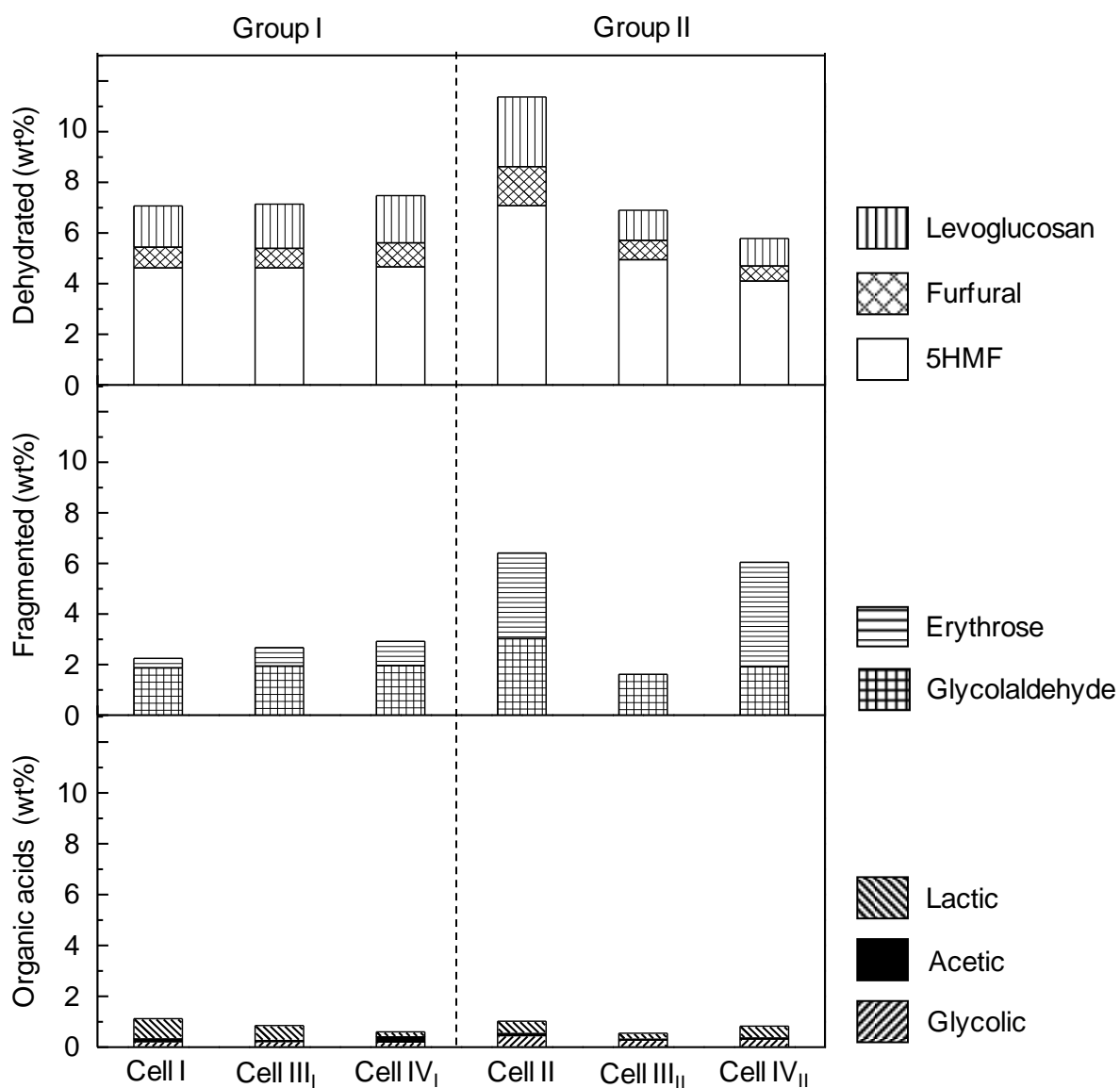


Fig. 6 The degraded products in WS portions from various types of crystalline celluloses as treated by semi-flow HCW at 270°C/10 MPa/15 min

Table 1 The crystallinity and *DP* for various types of crystalline celluloses prepared in this study

	Cellulose	Crystallinity (%)	<i>DP</i>
Group I	Cell I	92	176
	Cell III _I	86	164
	Cell IV _I	90	167
Group II	Cell II	85	173
	Cell III _{II}	87	176
	Cell IV _{II}	85	164

Table 2 The apparent activation energies of various types of crystalline celluloses as treated by semi-flow HCW at 230-270°C/10 MPa/15 min

	Cellulose	Activation energy, E_a (kJ/mol)
Group I	Cell I	71.4
	Cell III _I	78.0
	Cell IV _I	90.2
Group II	Cell II	53.3
	Cell III _{II}	59.0
	Cell IV _{II}	56.6

Table 3 The total hydrolyzed and degraded products of WS portions from various types of crystalline celluloses as treated by semi-flow HCW at 270°C/10 MPa/15 min

	Cellulose	Hydrolyzed product (wt%)	Degraded product (wt%)
Group I	Cell I	52.0	10.5
	Cell III _I	52.7	10.6
	Cell IV _I	67.0	11.1
Group II	Cell II	67.3	18.8
	Cell III _{II}	71.0	8.9
	Cell IV _{II}	67.0	12.6